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The Crystal Structure of a New Magnetic Ternary Boride $Nd_{0.71}Rh_{3.29}B_2$

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The structure of the ternary boride $Nd_{0.71}Rh_{3.29}B_2$ was determined by single-crystal X-ray diffraction. It has a hexagonal symmetry with space group $P\bar{6}2m$ and cell parameters $a = 5.595(2)$ and $c = 2.855(1)$ Å. Its structure is similar to that of the other $CeCo_3B_2$-type ternary borides. It is made up of two types of alternating layers, parallel to the (001) plane, formed by either (Nd,Rh) and B atoms or by Rh atoms alone.

Compounds containing rare earth elements, noble metals, and boron have been largely investigated, in particular those of the REM_4B_4-type structure. The close relationships between superconductivity, magnetism, and structural characteristics have been shown for the rhodium and iridium compounds (*1, 2*).

More recently, a number of ternary borides with general formula REM_3B_2 have also been studied and their magnetic and superconducting properties reported (*3, 4*).

The X-ray diffraction studies performed mainly on powder samples indicate that the REM_3B_2-type ternary borides (M = noble metal such as Ru, Rh, Ir, Os) may crystallize in one of three reported structures:

—(1) The $CeCo_3B_2$-type structure, which is adopted by most $RERu_3B_2$ compounds and by $RERh_3B_2$ for the larger RE ions (up to Gd).

—(2) The $ErIr_3B_2$-type structure, which characterizes the $RERh_3B_2$ (RE = Tb to Lu) and the $REIr_3B_2$ (except for La and Pr) phases.

—(3) The YOs_3B_2-type structure, which is found for the $REOs_3B_2$ (RE = Y, Sm, Gd, to Yb) borides.

All these structures are related to one another by deriving from the archetype $CaCu_5$ structure. Many other borides possess a $CaCu_5$-type derivative structure, such as the homologous series described by Kuz'ma and Bilonizkho (*5*) in the cerium–cobalt–boron system, and the ternary borides $MNi_{2.5}B_2$ (M = Mg, Li) reported by Jung (*6*). The $CeCo_3B_2$-type structure has a hexagonal symmetry with the reported space group $P6/mmm$ and derives from the $CaCu_5$-type structure by the replacement of the Cu atoms by Co and B atoms (*7–11*).

By replacing cobalt in the $RECo_3B_2$ structure by a 4d (Ru or Rh) or a 5d (Os or Ir) element Ku was able to prepare a series of compounds which showed superconductivity at temperature up to 4.6K for the nonmagnetic rare earths (La, Lu, Th) and magnetic ordering at temperatures up to 45K (*4*).

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Recently, Felner and Nowik have claimed the preparation of new hexagonal phases of the $RERh_6B_4$ type (or $RE_{0.5}Rh_3B_2$) (RE = Y, Lu, La, Eu^{3+}) with $a = 5.65$ and c: 17.1 Å (*12*). Our own X-ray diffraction studies have shown that the $RE_{0.5}Rh_3B_2$ spectra can be indexed in the $CeCo_3B_2$-type structure with no evidence at all indicating a sixfold multiplication of the c axis.

The fact that superconductivity, as well as magnetic ordering, has been observed for compounds such as $RERh_4B_4$ with spatially ordered local magnetic moments made it worthwhile to investigate this phenomenon for phases with the $CeCo_3B_2$-type structure containing ordered RE ions.

We therefore decided to study, as a first step, the homogeneity range and the accurate crystal structure of the $Nd_xRh_3B_2$ phases for which single crystals were easily obtained.

Experimental

1. Synthesis and characterization. The samples were obtained from mixtures of high-purity elements (Nd: 99.9%; Rh: 99.9%; B: 99.9%) pressed into pellets and melted in a tri-arc furnace under purified argon atmosphere. Weight losses of the samples during melting were negligible. Single crystals were taken from the obtained samples.

The powder diffraction patterns were perfectly indexed by isotypy with a $CeCo_3B_2$-type unit cell. Since at the nominal composition of $Nd_{0.66}Rh_3B_2$ a second minority phase was observed in the sample, a microprobe analysis was carried out in order to determine the composition of the single crystals. The observed ratio Nd : Rh was found to be 0.65(1) : 3. As we are dealing with a $CeCo_3B_2$-type compound, the formula can be expressed in two ways: (1) $Nd_xRh_3B_2$ and (2) $Nd_{1-x}Rh_xRh_3B_2$. They give rise to two different theoretical densities. The approximate observed density of the sample indicated without ambiguity the second model. The resulting composition can be written $Nd_{0.71}Rh_{3.29}B_2$. This was assumed to be the composition of the single crystal used in all our subsequent calculations.

2. Diffraction data. A single crystal was taken from the nonannealed sample for the X-ray diffraction study. The Weissenberg and Buerger photographs indicated the Laue symmetry $6/mmm$. No systematic absences were observed. This is consistent with the space group $P6/mmm$, $P\bar{6}2m$, $P\bar{6}m2$, $P6mm$, or $P622$. The lattice parameters of this crystal obtained from the refinement of a certain number of high-angle reflections on the diffractometer are a = 5.595(2) and c = 2.855(1) Å. In order to avoid an eventual two-phase region problem for the $Nd_{0.71}Rh_{3.29}B_2$ composition the accurate density was measured for the neodymium-poorer $Nd_{0.67}Rh_{3.33}B_2$ phase (as determined from microprobe). This value (9.94(2) g/cm³) should differ very little from that expected for $Nd_{0.71}Rh_{3.29}B_2$ and can be used for comparison. In fact, it is in good agreement with the calculated density of 9.92 g/cm³ for one formula per unit cell.

The intensity data collection was made with a crystal in the form of a thin plate (0.02 × 0.04 × 0.10 mm). These data were measured on a three-circle automatic diffractometer (E–N CAD-3) with Mo$K\alpha_1$ graphite-monochromated radiation (λ = 0.70929 Å) and a multiple $\theta/2\theta$ scanning technique up to $\theta_{max} = 45°$. After averaging the 12 equivalent reflections measured, 146 independent reflections were obtained ($I > 2\sigma(I)$) and corrected for the Lorentz and polarization factors, but not for absorption, $\mu r_{max} = 1.5$.

3. Structure determination. In the $CeCo_3B_2$-type structure with the space group $P6/mmm$ the RE atoms occupy the 1(a) position (000), the Co atoms the 3(g) position ($\frac{1}{2}0\frac{1}{2}$), and the B atoms the 2(c) ($\frac{1}{3}\frac{2}{3}0$). If we accept the composition of our crystal to be $Nd_{0.71}Rh_{3.29}B_2$, then the extra Rh atoms must occupy a site other than the normal 3(*g*) site. Two arrangements are possible:

—1. The extra Rh atoms occupy the 1(*a*) site together with the Nd atoms in a statistical distribution (Fig. 1a).

—2. The extra Rh atoms occupy a new 2(*e*) site 00*z*, $z \approx \frac{1}{4}$). This site seems to be the only one able to accommodate a rather large atom, such as Rh, even with a statistical distribution (see Fig. 1b).

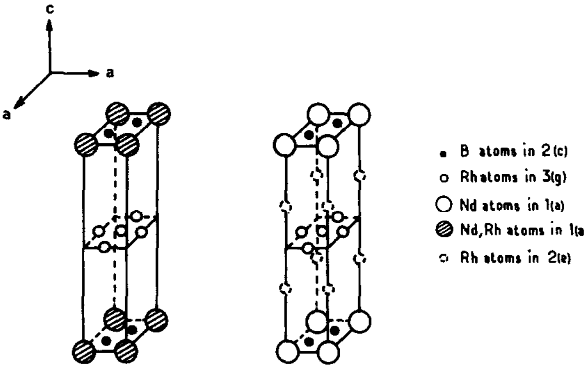
If the cell parameters can be an indication of the internal atomic arrangement, they can be used to predict the possible structure. If case 1 applies, the substitution of the larger Nd by the small Rh should *decrease* the *c* parameter size. If, on the contrary, case 2 applies, then the introduction of the extra Rh atoms along the *c* axis should *increase* the *c* parameter. In fact, the *c* parameter of $NdRh_3B_2$ (3.109 Å) is much longer than the corresponding value for $Nd_{0.71}Rh_{3.29}B_2$ (2.855 Å). If no other factors are involved, case 1 should be the arrangement adopted.

The study of 3D–Patterson synthesis definitely confirmed this hypothesis. Besides this confirmation, the observed Rh–Rh vectors in the 3D Patterson indicate clearly and without ambiguity that only the space group $P\bar{6}2m$ can produce Rh–Rh vectors compatible with the observed ones. In the new space group the (Nd, Rh) atoms occupy the 1(*a*) (000) site with a statistical distribution. The boron atoms are found on the 2(*c*) ($\frac{1}{3}\frac{2}{3}0$) site and the normal Rh atoms are placed on the 3(*g*) ($x0\frac{1}{2}$, $x \approx 0.51$) site. The structure described in the space group $P\bar{6}2m$ is little different by comparison to the old description and differs only in the position of the Rh atom, which has its *x* parameter equal to 0.51 instead of $\frac{1}{2}$.

Several cycles of anisotropic least-squares refinement using a full-matrix algorithm led to an *R* factor of 8% (*13*). The scattering factors for Nd, Rh, and B were those of McMaster *et al.* (*14*). The scattering factor of the composite atom (Nd, Rh) were calculated by a weighted mixture (0.71 Nd + 0.29 Rh) of the individual atoms. Tables I and II give, respectively, the atomic parameters and the interatomic distances.

Discussion

The atomic arrangement in the $Nd_{0.71}Rh_{3.29}B_2$ lattice is shown in Fig. 2. The structure is made up of two types of infinite



Case 1
(a)

Case 2
(b)

FIG. 1. Two possible structural models for the substitution of Rh into the $NdRh_3B_2$-type structure.

TABLE I

POSITIONAL PARAMETERS AND ANISOTROPIC TEMPERATURE FACTORS FOR $Nd_{0.71}Rh_{3.29}B_2$ (esd IN PARENTHESES)

Atom	x	y	z	U_{11} (Å^2 × 10^4)	U_{22}	U_{33}	U_{12}
(Nd, Rh)	0	0	0	181(14)	U_{11}	377(29)	$U_{11/2}$
Rh	0.5052(7)	0	$\frac{1}{2}$	67(6)	58(8)	8(5)	$U_{22/2}$
B	$\frac{1}{3}$	$\frac{2}{3}$	0	447(305)	U_{11}	17(120)	$U_{11/2}$

Note. The temperature factor expression is: $\exp[-2\pi(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + hka^*b^*U_{12} + hla^*c^*U_{13} + klb^*c^*U_{23})]$.

layers, parallel to the (001) plane. One layer contains the (Nd, Rh) and B atoms and the other Rh atoms alone (Figs. 2a and b). These layers, perpendicular to the [001] direction and separated by a distance $c/2$, alternate with one another to form the three-dimensional lattice.

The occupation of the normal Nd site by two different atoms in a statistical way, although not usual, has been observed elsewhere for $La_{0.5}Y_{0.5}Rh_3B_2$ (*4*). This can be explained by the large volume of this site, particularly in the (001) plane (Fig. 2a), where its boron atom neighbors are small in size and no direct Nd–B bonding occurs ((Nd, Rh)–B = 3.230 Å; radii sum = 2.70 Å).

The bonding scheme in the structure is accomplished by direct intralayer and interlayer Rh–Rh bonds of 2.798 and 2.855 Å, respectively, and by strong Rh–B bonding (2.156 Å) between adjacent layers. The Rh–Rh distances are slightly longer than the metallic radii sum (2.68 Å), whereas the Rh–B distances are somewhat shorter with respect to the radii sum (2.22 Å). These distances compare well with those observed in Rh_5B_4 (*15*). Additional direct (Nd, Rh)–Rh interlayer bonding is observed (3.167 and 3.115 Å) close to the weighted radii sum (3.02 Å) and is indicative of metallic-type bonding. However, there seems to be no significant bonds formed between the (Nd, Rh) and the B atoms ((Nd, Rh)–B = 3.230 Å). The rare earth atoms are thus only bonded to the rhodium atoms in adjacent layers with the exception of a rather short (Nd; Rh)–(Nd, Rh) bond (2.855 Å) between two neighboring atoms along the c-axis direction in adjacent cells. This distance,

TABLE II

INTERATOMIC DISTANCES (Å) (esd IN PARENTHESES)

2 × Nd–Nd[a]	2.855	4 × Rh–Rh	2.798(3)	2 × B–B	2.855
6 × Nd–Rh	3.167(1)	2 × Rh–Rh	2.855(3)	3 × B–B	3.231
6 × Nd–Rh	3.115(1)	4 × Rh–B	2.156(1)		
6 × Nd–B	3.230				

[a] Nd represents the composite (Nd, Rh) atom (Nd and Rh are statistically distributed on the same site).

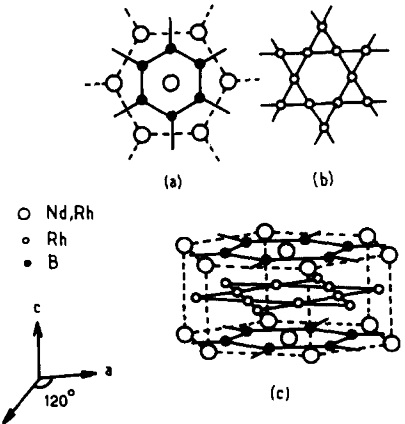


FIG. 2. Structure of $Nd_{0.71}Rh_{3.29}B_2$: (a) (Nd, Rh) and B atom layer perpendicular to the c axis; (b) Rh atom layer perpendicular to the c axis; (c) stacking of the (a) and (b) layers to form the crystal lattice.

which is much shorter than the weighted radii sum (3.36 Å), assumes strong metallic-type interactions and the formation of metal–metal infinite chains along this direction.

The coordination polyhedra of the various atoms in the lattice are somewhat unusual with the Nd atom surrounded by 12 Rh atoms forming a hexagonal prism along the (001) direction. Moreover, the Rh atom is found in a 10-fold coordination surrounded by a Rh octahedron capped on four of its faces by a boron atom. Finally, the boron atom has a trigonal prismatic environment of rhodium atoms.

In conclusion, our study has corroborated the general structural features of a $CeCo_3B_2$-type compound and has provided accurate bond distance information. The phase $Nd_{0.71}Rh_{3.29}B_2$, which is part of the homogeneous region $Nd_{1-x}Rh_xRh_3B_2$ included between $x = 0.29$ and $x = 0.52$, seems to be a new ternary boride with a different space group ($P\bar{6}2m$). This is indicated by the existence of a multiphase region for $0 < x < 0.29$. Whether the phase $NdRh_3B_2$ ($x = 0$), with the supposed space group $P6/mmm$, has exactly the same structure is difficult to conclude since this choice was made on the basis of powder X-ray diffraction data only, which do not permit any detailed structural features to be determined (*4*). Of equal importance is the observed substitution of the Nd site (1(*a*)) by a noble metal of similar size.

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